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THz Generation and Detection by Fluorenone Based Organic Crystals

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Supporting Information

ABSTRACT: Direct study and control of material properties using terahertz (THz) frequency pulses is an emerging subject with strong potential for future applications. One aspect of the development of THz-based techniques is the search for new materials that can efficiently convert higher frequency light into the THz-frequency range and serve to detect and characterize weak THz radiation with high sensitivity. Here, the capabilities of a new class of THz generators and detectors based on diphenylfluorenone (DPFO) crystals are explored. We demonstrate that DPFO crystals have an extremely large electro-optical coefficients centered at around $f \approx 1.5$ THz which makes them ideal for THz detection at this frequency. Excitation with intense femtosecond near-infrared pulses leads to emission of narrow-band ($\Delta f/f \approx 20\%$) THz radiation near 1.5 THz. This frequency range does not overlap significantly with water vapor absorption lines, which allows for practical applications under ambient conditions.

KEYWORDS: electro-optics, nonlinear optics, organic crystals, terahertz waves

THz radiation is of increasing interest for a broad range of scientific and technological applications.¹ In solid-state physics and material science, the frequency region between 0.1 and 20 THz matches the energy range for different excitations of high interest in material science, such as polarons, excitons, phonons, and magnons. In this context, THz radiation has become a powerful tool to study semiconductors,² magnetic materials,³ superconducting states,⁴ and charge density waves.⁵ In recent years, the possibility to control material properties with intense THz pulses has attracted considerable interest. This capability has been demonstrated for a range of phenomena, spanning phase transitions,⁶ ferroic order excitations,⁷ magnetization dynamics,^{8–13} ferroelectric excitations,^{14,15} superconductive properties,¹⁶ as well as linear and nonlinear excitations of phonons.^{17–21} These innovative works have motivated research into developing stronger and tunable THz sources, which allow for new methods of light-induced control relevant not only for fundamental research but also for future technologies.^{22–24}

One method to generate high-power THz pulses is to propagate an intense femtosecond near-infrared laser pulse through a material with large second-order nonlinear optical susceptibility ($\chi^{(2)}$). The generated second-order nonlinear optical response has a component in the THz range with a frequency content related to the envelope of the femtosecond pulse inside the material, a process known as optical rectification (OR). Initially, this phenomenon was exploited

in inorganic compounds, such as CdTe, ZnTe, GaP, and LiNbO₃,²⁵ which offer good stability, transparency, and robustness to intense optical pulses in the near IR. Their main drawback is a rather low yield of THz peak fields (typically significantly lower than 100 kV/cm in CdTe, ZnTe, GaP), unless relatively complex schemes like pulse-front tilting are used.²⁵ In comparison to these inorganic crystals, polar organic materials have emerged as an attractive alternative owing to their generally much higher $\chi^{(2)}$ values. Prominent examples include (2-(3-(4-Hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile) (OH1), 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate (DSTMS), and 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazoliumtosylate (DAST).^{26–32} More recently, some new families of organic compounds have been proposed, such as the quinolium-based (HMQ) compounds.^{33–37} These organic molecular materials have been used to generate THz peak fields approaching the benchmark level of 1 MV/cm in the 0.8–4 THz range.^{38–41} Currently, there are two main drawbacks with these organic materials: (i) it is challenging to grow large crystals without defects and (ii) they are less robust than inorganic compounds against strong optical pumping.

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In an attempt to find more robust alternatives, we have investigated a series of promising nonlinear optical organic crystals based on fluorenone derivatives.^{42–44} These fluorenone-based compounds feature multiple synergistic non-covalent interactions that drive the formation of non-centrosymmetric dipolar supramolecular arrangements. These crystals have demonstrated very large nonlinear optical coefficients for second harmonic generation comparable to those of KH_2PO_4 (KDP) and LiNbO_3 ,^{42–45} as well as a very high laser damage threshold, for excitations in the 700–900 nm range.⁴⁴ One of the building blocks of these compounds, namely, the diphenylfluorenone (DPFO), can be readily grown into large size crystals (typical surface area $5 \times 5 \text{ mm}^2$, thickness range: 50–150 μm) via simple solution based processes at ambient conditions, driven by the synergistic hydrogen-bonds and $\text{C-H}\cdots\pi$ interactions.^{42,43} In its crystal phase, the molecules stack into an orthorhombic unit cell belonging to the $C_{2m}2_1$ space group. The growth process of DPFO crystals is highly anisotropic, with the fastest growth directions being the crystallographic a - and c -axes. The most efficient second-harmonic generation (SHG) for near-infrared pulses occurs when the incident light is polarized parallel to the c -axis, the direction of the cumulative permanent electric dipole of the DPFO molecules.^{42,43}

In view of the extraordinary high $\chi^{(2)}$ values for second harmonic generation from these crystals,^{42–45} we have investigated in this work the potential in using them for THz generation and detection. In a first step we determined the refractive indices in the THz frequency range as a function of the sample orientation, by performing THz time domain spectroscopy⁴⁶ (TDS) with a setup sensitive to the 0.5–2.2 THz spectral range. This experimental configuration is based on GaP Electrooptic (EO) detection of THz pulses generated through optical rectification of 1.3 μm radiation in OH1 (for more details, refer to [Experimental Methods](#) and refs 46–50).

Figure 1a shows the measured DPFO spectra for a few sample orientations (positive and negative rotations correspond to solid and dashed lines, respectively) compared to the reference measurement (no sample, solid black line). By rotating the sample we span the ac -plane, while the b -axis is parallel to the light propagation direction. From these spectra, we determine the refractive index along the different crystallographic axes (Figure 1b), with an approximate uncertainty of $\pm 5\%$. Interestingly, both components of the refractive index, $n(\omega)$ and $k(\omega)$, increase around $f = 1.5 \text{ THz}$ when the incident THz radiation and the permanent dipole align, $E_{\text{THz}} \parallel c$ -axis, (solid lines); this feature is absent for $E_{\text{THz}} \parallel a$ -axis (dashed lines). At this frequency, the sample is both optically denser and more absorbing along the permanent dipole axis (c -axis). Figure 1c presents the measured transmission through the DPFO sample at $f = 1.5 \text{ THz}$ as a function of polarization relative to the c -axis. The solid line represents the best fit to the function $T_{\text{avg}} - A \cos\left[\frac{\theta}{2} + \phi\right]$, where T_{avg} is the averaged transmission at 1.5 THz, A the amplitude of the modulation, θ the angle in radians between the permanent dipole direction (c -axis) and the THz E-field polarization (fixed), and ϕ an angular correction to account for systematic uncertainty in determining the c -axis direction. For the fit shown in Figure 1c, the best-fit parameters are $T_{\text{avg}} = 0.63$, $A = 0.075$, and $\phi = 11^\circ$.

We now turn to the nonlinear optical properties of DPFO, focusing first on the use of DPFO as an electro-optical detector for THz fields. Figure 2 presents the comparison between EO

Figure 1. (a) Measured THz spectrum after absorption in DPFO obtained through EO sampling in GaP of THz broadband pulses generated in OH1 via optical rectification. The spectra are shown for different sample orientations in the ac -plane (positive and negative angles, represented by solid and dashed color lines respectively) and compared to the reference measurement (no sample, black solid line). (b) Extracted n (red) and k (blue) components of the refractive index. Solid line: THz polarization $\parallel c$ -axis; dashed line THz polarization $\parallel a$ -axis. (c) Transmission through the DPFO sample at $f = 1.5 \text{ THz}$ for different sample rotations. The blue curve shows the results of a fit described in the text.

Figure 2. Comparison between EO detection in GaP and DPFO, normalized by the crystal thicknesses. The same THz pulse is incident on the two crystals, generated via OR in OH1. Inset: Spectrum of the detected radiation.

detection in a 300 μm -thick GaP and a 50 μm -thin DPFO of a broadband single cycle THz pulse generated by OH1. The detected traces are normalized by the crystal thickness. In this measurement, the transient electric field of the THz pulse

Table 1. Maximum Value for the EO Coefficient r in the 0.5–4 THz Frequency Range for Most Common THz Generation Crystals and DPFO

material	GaP	ZnTe	LiNbO ₃	DAST	DSTMS	OH1	DPFO
r_{max} (pm/V)	1	4	28	47	49	52	74

induces a transient birefringence in GaP (or DPFO) via the EO effect. This birefringence causes a change in polarization of the 100 fs, 800 nm pulses that results, after polarization analysis optics, in a change in detected intensity ΔI . For a sufficiently thin crystal and sufficiently short probe pulse ΔI is given by^{51,52}

$$\Delta I(t)/L \propto \beta E_{\text{THz}}(t)/L = \frac{2\pi n_{\text{IR}}^3 r}{\lambda_{\text{IR}}} E_{\text{THz}}(t) \quad (1)$$

with r the EO coefficient, L the crystal thickness, n_{IR} the refractive index of the material at the near-infrared probing wavelength λ_{IR} , and $E_{\text{THz}}(t)$ the THz field generated by OH1. DPFO shows a 4× larger response than GaP at 1.5 THz. Equation 1 is valid in the limit that the entire sample thickness L is involved in the detected response, which implies a good phase matching between the THz and the IR beams. For ideal phase matching⁵³

$$\Delta k = k(\Omega_{\text{THz}}) + k(\omega_{\text{IR}}) - k(\omega_{\text{IR}} + \Omega_{\text{THz}}) = 0 \quad (2)$$

where k is the wavevector of the copropagating radiations at THz (Ω_{THz}) and near-IR (ω_{IR}) frequencies, respectively. Since $\Omega_{\text{THz}} \ll \omega_{\text{IR}}$ and both beams are collinear, eq 2 reduces to a matching condition between the phase velocity of the generated THz radiation ($v(\Omega)$) and the group velocity of the near-IR pump pulse ($v_g(\omega)$). Fulfillment of the phase matching condition therefore depends on the radiation frequencies and for an anisotropic material on the crystal orientation. For DPFO optimum phase matching is obtained around $f = 1.5$ THz for $E_{\text{THz}} \parallel c$ (DPFO shows a group refractive index $n_g^{\text{IR}} \approx 1.47^{44}$ and refractive index $n_{\text{THz} \parallel c} = 1.37$, while $n_{\text{THz} \parallel a} = 1.27$), or for $f < 1.0$ THz. At $f = 1.5$ THz, we estimate a coherence length $L_c = |2\pi/\Delta k| \approx 1$ mm for $E_{\text{THz}} \parallel c$ and $L_c \approx 0.5$ mm for $E_{\text{THz}} \parallel a$, respectively. At higher frequencies n_{THz} decreases, hindering the phase matching conditions. For comparison in GaP L_c is larger than 5 mm.^{26,27,54}

Using eq 1 and taking into account reflection losses and the materials' refractive indices, we can compute the EO coefficient r . In the following we will consider the coefficient r_{zzz} , the largest element of the EO tensor in DPFO crystal group symmetry. For GaP we assume a flat response in the frequency range under investigation^{55,56} and calculate $r = 0.98$ pm/V, well in agreement with the reported value of $r = 1$ pm/V.^{26,27,55,56} In the case of DPFO, we can estimate r from the ratio of the spectral response given by the inset of Figure 2 and taking into account the different reflectivity of these crystals compared to OH1. We estimate a value of 74 pm/V for frequencies near 1.5 THz for $E_{\text{THz}} \parallel c$ -axis, 2 orders of magnitude larger than that of GaP. At lower frequencies, the value of r quickly drops even though n_{THz} approaches n_{NIR} . For completeness we compare in Table 1 the maximum values for r in the frequency range under investigation for the other common THz crystals.^{26,27,53,57} DPFO clearly shows the largest EO coefficient value, thus making it attractive for sensitive detection of weak THz signals around 1.5 THz.

The value of the EO coefficients r_{ij} are directly related to the second order polarizability tensor $\chi_{ij}^{(2)} = -0.5n_i^2 n_j^2 r_{ij}$,⁵⁰ where i and j indicate the direction of polarization of the input beams. In particular, DPFO and OH1 share the same space group

symmetry, for which the largest second order activity occurs when $i = j = z$ (the c -axis). In this case the relation simplifies to $\chi_{zz}^{(2)} = -0.5n_z^4 r_{\text{max}}$. Because of the larger refractive index ($n_{\text{OH1}} = 2.3$; $n_{\text{DPFO}} = 1.47$), the second order polarizability is roughly 4× larger in OH1.

The large EO-coefficient in the proximity of 1.5 THz and the good phase matching conditions offers efficient THz generation via optical rectification in this frequency range. Figure 3a shows

Figure 3. (a) Comparison of THz emission normalized by crystal thickness of DPFO and OH1 in the low THz region (up to 2.5 THz), detected via EO sampling in a GaP crystal. Inset: Spectrum of the generated THz. DPFO is characterized by narrow band emission at 1.5 ± 0.15 THz. Emission from DPFO is only comparable to the one from OH1 around 1.5 THz, while being negligible otherwise. (b) Logarithmic plots of the generated peak THz field as a function of fluence. Above 50 mJ/cm² both crystals start exhibiting surface damage.

the direct comparison of the emission between OH1 and DPFO crystals in the low THz region, for a pump wavelength $\lambda = 1350$ nm. No significant differences in the DPFO emission have been measured in the $\lambda = 1150$ – 1500 nm range (see also Figure S2), but no THz emission was observed with $\lambda = 800$ nm. To account for the difference in thickness, the detected emission is normalized by the propagation distance through the crystals. It is apparent that the THz generation from DPFO is comparable with OH1 only at the specific frequency of $f = 1.5 \pm 0.1$ THz. Within the remaining part of the 0.3–2.5 THz range, the emission of DPFO is negligible. Excitation of the crystal with polarization perpendicular to the c -axis results in a much weaker (<50%) THz emission. Such a relatively strong and narrowband ($\Delta f/f \approx 20\%$ bandwidth) emission could make DPFO, upon optimization, an attractive source for applications

where narrowband multicycle THz pulses centered at 1.5 THz are desirable. Note that this efficient emission band lies between the strong water vapor absorption lines at 1.4 and 1.7 THz,⁵⁸ making long distance air propagation possible with little attenuation from ambient humidity.

To further compare the THz generation of DPFO and OH1 crystals we have measured the emitted field as a function of the laser fluence transmitted through the first interface. The excitation conditions were identical in terms of laser wavelength, polarization and pulse duration. Figure 3b presents the peak field amplitude (normalized once again by the generating volume thickness). We chose a logarithmic scale to enhance the visibility of deviations from the linear behavior. For both crystals a slight deviation from linearity is measured with fluences ≥ 10 mJ/cm². Although not markedly different, DPFO shows a slightly broader range of linearity in the THz generation process. On the other hand, DPFO performs worse at larger optical excitations. For both crystals, in fact, visible surface damage appears for fluences > 50 mJ/cm². At this stage DPFO shows a strong saturation of the emitted THz radiation followed by surface deformation, in turn causing an overall decrease in generation (≥ 80 mJ/cm²). In the same range OH1 exhibits clear surface damage, with a slow saturation of the emitted THz. Overall the crystals feature a rather similar behavior as a function of excitation fluence. Most of the heat generated in the optical rectification process comes from multiphoton events, since both crystals present a featureless and weak (< 1 cm⁻¹) absorption coefficient in the 700–1400 nm range (500–1500 nm for DPFO).^{42,59,60} Multiphoton effects typically limit the extent of the absorption to only a fraction of the exposed volume. The remaining part of the sample can thus act as a sink of excess heat. In this respect DPFO behaves similarly to OH1, but as the measured crystals are notably smaller than commercially available OH1, a much larger increase in temperature may be expected. Thus we foresee that larger crystals, once produced possibly by extremely slow cooling processes (< 1 °C day⁻¹),^{29,33} could show better performance in terms of optical power resilience.

We have also measured the emitted THz radiation using a different method, namely Air-Biased Coherent Detection (ABCD),^{61,62} to study the emission characteristics of DPFO crystals up to 15 THz. Figure 4 presents the emission spectra

Figure 4. Broadband THz emission, as measured with the ABCD method. The IR polarization was tuned to be parallel to the *c*-axis (black) and *a*-axis (red). Inset: Simulated spectra of THz activity for molecular building blocks of DPFO crystals.

upon excitation along the crystallographic *a*- and *c*- axes of a 50 μ m thick crystal). Considering at first the case when the IR pulses are polarized along the *c*-axis ($E_{\text{IR}} \parallel c$ -axis, black line), a pronounced feature at $f = 1.5$ THz is clearly visible. Moreover, a broadband emission up to 12 THz is detected. In addition to the broadband emission two other peaks can be identified, at $f \approx 2.5$ and 5 THz. Similar spectra were obtained when tuning the excitation wavelength from 1100 to 1550 nm (see Figure S1 in Supporting Information). Conversely, when E_{IR} is parallel to the *a*-axis (red line), we observe a decrease of the emission at 1.5 THz, and a strong increase at $f \approx 2.5$ THz. Moreover, the contribution at higher frequencies ($2.5 < f < 12$ THz) vanishes. Further studies (along the lines of ref 63, for example) could show additional capabilities in the multi-THz regime.

In order to achieve a deeper understanding regarding the microscopy origin of the THz activity, model calculations have been performed (see Experimental Methods for details). Initially a harmonic terahertz spectrum for an isolated single molecule of DPFO was calculated using Density Functional Theory (DFT). The resulting stick spectrum is visualized in black in the inset of Figure 4. In this frequency range, vibrations are likely to have a strongly anharmonic character. Unfortunately, calculations of anharmonic spectra for this molecule size are prohibitively expensive. We thus performed classical molecular dynamics simulations of both a single molecule and of the crystal structure. The orange curve shows the resulting spectrum for a single molecule at 300 K. Some shifts as compared to the harmonic spectrum can be observed, as well as differences in intensities. Also, new transitions appear, indicative of the anharmonicity in the vibrations. The red curve shows instead the generated THz spectrum for the crystalline structure based on the dipole changes within the *ac*-plane. For all spectral features, a blueshift and a line broadening with respect to the single molecule spectrum (orange) can be observed as a consequence of a mixing of intermolecular and intramolecular vibrations. This set of simulations show a peaked generation at 1 and 2 THz, which may be identified with the experimentally measured peaks at 1.5 and 2.5 THz, plus a broadband emission above 3 THz, also verified experimentally. Aside from the frequency shift mentioned above, the spectral features and distribution are in a reasonable agreement with the experimentally measured THz generation. In particular, we can ascribe the lowest frequency (1.5 THz) to a scissoring around the *a*-axis, while the peak at 2.5 THz is associated with a twisting along the *c*-axis of the DPFO molecules (animations showing the molecular motion are available online). The measured spectral features can therefore be ascribed to specific molecular vibrations of the building blocks of DPFO crystals.

In conclusion, we have demonstrated that the diphenyl-fluorenone (DPFO) based molecular crystal exhibits a larger EO coefficient r than those reported for common THz crystals in a narrow range of frequencies, $f = 1.5 \pm 0.1$ THz, which makes it suitable for narrowband or multicycle THz detection applications. It shows, moreover, a strong emission feature at 1.5 THz, connected to molecular vibrations associated to the building block of these crystals, as demonstrated with classical molecular dynamics simulations. DPFO therefore constitutes a narrowband source (20% bandwidth), with THz field strength comparable to OH1, which could be used for selective probing and pumping at this specific frequency. This is valid even at ambient conditions, since water absorption lines do not significantly affect the emitted spectrum.

■ EXPERIMENTAL METHODS

Sample Preparation. DPFO was synthesized following the procedures reported in previous work.⁴² The compound has been characterized by ¹H and ¹³C NMR, MS, and elemental analysis. The DPFO crystals suitable for THz measurements have been readily grown by direct evaporation of the solvent from its saturated solution in toluene at ambient conditions.

High-Sensitivity Narrowband Setup for TDS. The output of a Ti:Sapphire amplifier ($\lambda = 800$ nm, repetition rate: 1 kHz, average pulse energy $E = 1.8$ mJ) is sent into an optical parametric amplifier (OPA) to generate longer wavelength light pulses ($\lambda_{\text{OPA}} = 1350$ nm, typical average pulse energy $E = 0.25$ – 0.3 mJ). In a second step, intense nearly single cycle THz pump pulses were generated via optical rectification of the infrared output of the OPA in an OH1 or DPFO crystal. After filtering out the residual infrared beam, two off-axis parabolic mirrors (PM) are used to collimate, and then focus the THz beam onto the sample. A small amount of the 800 nm light (<1%) is picked off before the OPA to be the probe beam. It is focused with a 150 mm lens to a spot size of $d \approx 22$ μm fwhm at the sample position. With this arrangement, we can routinely achieve field strengths, at the focus position, exceeding 250 kV/cm (zero to peak) in a dry atmosphere. The probe beam experiences a transformation of its polarization state from linear to elliptical by interacting with the GaP substrate due to the THz-induced electro-optic (EO) effect.⁵³ A quarter wave plate and a Wollaston prism together with a balanced amplifier photodetector collect the signal and its polarization changes as a function of the relative delay between the pump and probe.

Broadband THz Detection with ABCD Method. The Air-Biased Coherent Detection (ABCD)^{61,62} is employed to measure THz-emission from DPFO crystals in the 0.5–15 THz range, resulting from excitation with short IR pulses generated by an optical parametric amplifier (central wavelength $\lambda \approx 1350$ nm, typical pulse duration $\tau \approx 75$ fs). For details on our experimental setup, please refer to ref 64.

Theoretical Simulations. A harmonic terahertz spectrum of a single molecule was calculated using DFT (B3LYP/6-31G*) using Molpro.⁶⁵ The classical molecular dynamics simulations of the single molecule and the crystal structure were performed using LAMMPS (version 16–02–2016).⁶⁶ The force field GAFF2.1 was used for the intra- and intermolecular interactions⁶⁷ in combination with point charges fitted to the electrostatic potential. These point charges were calculated with the help of Molden,^{68,69} where the electrostatic potential was obtained using the results of the aforementioned DFT calculations. For both single molecule spectra, the purely rotational features have been removed. The simulation cell consists of $4 \times 2 \times 4$ crystallographic unit cells (64 molecules). Simulations are performed in the triclinic NPT ensemble. The orthorhombic character was retained during the simulations giving confidence to the applied force field.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsp Photonics.7b00792.

THz properties in the multi-THz region (PDF).

Movie S1: THz vibrations of DPFO molecules, at the excitation frequency we have associated with the 1.5 THz spectral features (AVI).

Movie S2: THz vibrations of DPFO molecules, at the excitation frequency we have associated with the 2.5 THz spectral features (AVI).

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Notes

The authors declare no competing financial interest.

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